QUANTITATIVE ANALYSIS OF KINETIC ENERGY SHIFTS IN MASS-ANALYZED ION KINETIC ENERGY SPECTRA (MIKES)

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: الخلاصـــة

تَمَّ قياس الطاقة الحركية التي تنقل ايونات الشظايا المنشطة بالتصادم من حجرة التصادم المعوَّمة كهربائيا بواسطة فوتومتر طيفي يعمل بنظام ترادف الكتلة لعدد من المركبات وهي : ن – ديدوكين ، وبيرفلوروكيروسين ، وكيومين . ولقد تم مقارنة هذه القياسات مع قياسات أخرى اعتمدت على حساب طاقات التحولات الشبه مستقرة . ولأنه من المعروف أن القياسات المخبرية دائماً تكون أقل من المتوقعة بنسب ضئيلة ، مما أدى إلى الظن بأن الطاقة المنقولة الى الجزىء المستهدف يمكن أن تكون أكبر مما هو متوقع بعد الأخذ بعين الاعتبار ترسيب أكبر طاقة داخلية . وقد وُجد أن فعالية التفتيت لمركب (الكيومين) في هذه التصادمات ذات الطاقة العالية تتراوح مابين (٧٤٪ الى ٨٨٪) وهذا يماثل طريقة استخدام مقطع تصادمي ذي مجال ضيق (٣ × ١٠⁻¹⁴ سم²) . ومن ناحية أخرى وجد أن عملية تفتيت الايونات التوجة (Parent ions) تعتمد في الدرجة الاولى على ضغط غاز الهيليوم والمقـدَّر بحوالي (٣ × ١٠⁻⁶ / تور) ، وثابت معدل حوالي (٠,٨٧ × ١٠⁻⁶ / تور) .

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ABSTRACT

Kinetic energy shifts of collisionally activated fragment ions from an electrically floated collision chamber in an EBE tandem mass spectrometer are measured for n-dodecane, perfluorokerosene, and cumene, and compared with those calculated based on the energetics of metastable transitions. It is determined that the experimental values are always a few percent smaller than the predicted ones, suggesting that the translational energy transfer to the target molecules may be larger than generally believed, after taking the largest internal energy deposition into account. The fragmentation efficiency for cumene in these high-energy collisions ranges from 74 percent to 88 percent, corresponding to a narrow range of collisional cross-section of around $3 \times 10^{-14} \, cm^2$. The fragmentation processes of the parent ions, on the other hand, undergo a pseudo-first-order dependence on a target helium pressure of within 3×10^{-6} torr, with a rate constant of $0.87 \times 10^6 \, torr^{-1}$.

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INTRODUCTION

Selected ion fragmentation in tandem mass spectrometry is one of the most informative areas in mass spectrometric research [1]. The precursor ion is mass-selected, fragmented with target gas, and the resulting fragment ions are energy-resolved by using an electrostatic scan. The internal energy released to ions of 5 kV in the presence of helium gas of up to 10^{-5} torr in the collision cell in these collisionally activate dissociations (CAD) has been observed to be on the order of one eV in some biomarkers in crude oils [2]. Thus, the energetics of CAD appears similar to that of metastable transition in regard to the conversion of vibrational energy [3]. It is generally believed, nonetheless, that kilovolt collisions involve electronic excitation, while low-energy collisional activation proceeds via vibration/translational energy transfer [4]. In order to observe the consequence of electronic excitation during high-energy collisions and to differentiate those daughter ions formed in the collision cell from those formed outside the cell which presumably dissociate unimolecularly, floated potentials are applied to the cell [5–8]. It is those cells that offer the possibility of investigating the kinetic energy shift (*KES*) of the ions following their interaction with the collision gas. These shifts can be explained qualitatively by the retardation and acceleration processes occurring inside the cell depending on the polarity of the cell voltage [9, 10]. Since no systematic results are available as yet to account quantitatively for these shifts with respect to the theoretical prediction, it is our intention in this work to correlate them and to take it as a caliper for modifications in future investigations.

EXPERIMENTAL

All the MIKES were obtained from the JEOL HX100 trisector (E_1BE_2) tandem mass spectrometer with acceleration voltage, $V_a = 5$ kV. The precursor ions were first mass-analyzed and sensitivity maximized by E_1B without a collision chamber. Then the cell was engaged without target gas to again adjust the resolution and sensitivity with slits and field on E_2 under E_2 mode, insuring that E_2 can be scanned while E_1 and B are fixed. Minimal magnetic field drift and imprecise E_2 field were the major causes for the drastic signal amplitude changes towards low sensitivity. For all of the experiments, electron

energy of 70 eV and ion multiplier (IM) voltage of -2.5 kV were used. The width of the energy resolving slit was set at 3.01 mm. Since the average internal energy of positive ions depends on the ion source temperature [11], all the experiments were undertaken at source temperature of 170°C. Helium with nominal pressure of 10^{-5} to 10^{-6} torr was used as target gas to obtain reasonable ratios of parent to daughter ions. The pressure was read from a Penning gauge located between the cell and the diffusion pump in the third field free region (FFR3). The real pressure inside the cell might be significantly higher depending on the conductance of the pumping line. Floated potential of collision cell could be varied within ± 20 kV. Accumulation of around 20 scans was performed for each experiment to acquire representative spectra before the sample was consumed.

The chemicals employed in this study were n-dodecane, isopropylbenzene (cumene), and perfluorokerosene (PFK). One microliter each was separately introduced into the reservoir of the mass spectrometer inlet system.

RESULTS AND DISCUSSION

1. Fundamental of Energetics in a Perturbed Ion Flight Path and the Experimental *KES*

Under well-tuned conditions, there is an intrinsic decrease in signal-to-noise ratio (S/N) of around three to ten, depending on the nature of the parent ion and the compound when the collision chamber is in the ion path. The MIKES of 219^+ of PFK in Figures 1 and 2 demonstrated this effect. It is, perhaps, a simpler system for one to observe the *KES*, since peaks 69^+ and 131^+ appear to be the major daughter ions and there is no peak overlap.

Suppose that an ion m_1^{+z1} decomposes in the field-free region along a tandem mass spectrometer flight path, yielding a daughter ion m_2^{+z2}. If this dissociation takes place with negligible conversion of excitation energy into kinetic energy, each daughter ion m_2^{+z2} will continue to move along the original direction of motion of its m_1^{+z1} and with the same velocity, which is typical of metastable transition. There are several important consequences that result from this simple fact. Energy will be shared between fragments in the ratio of their masses. That is, the kinetic energy ratio of daughter to parent ion is m_2/m_1.
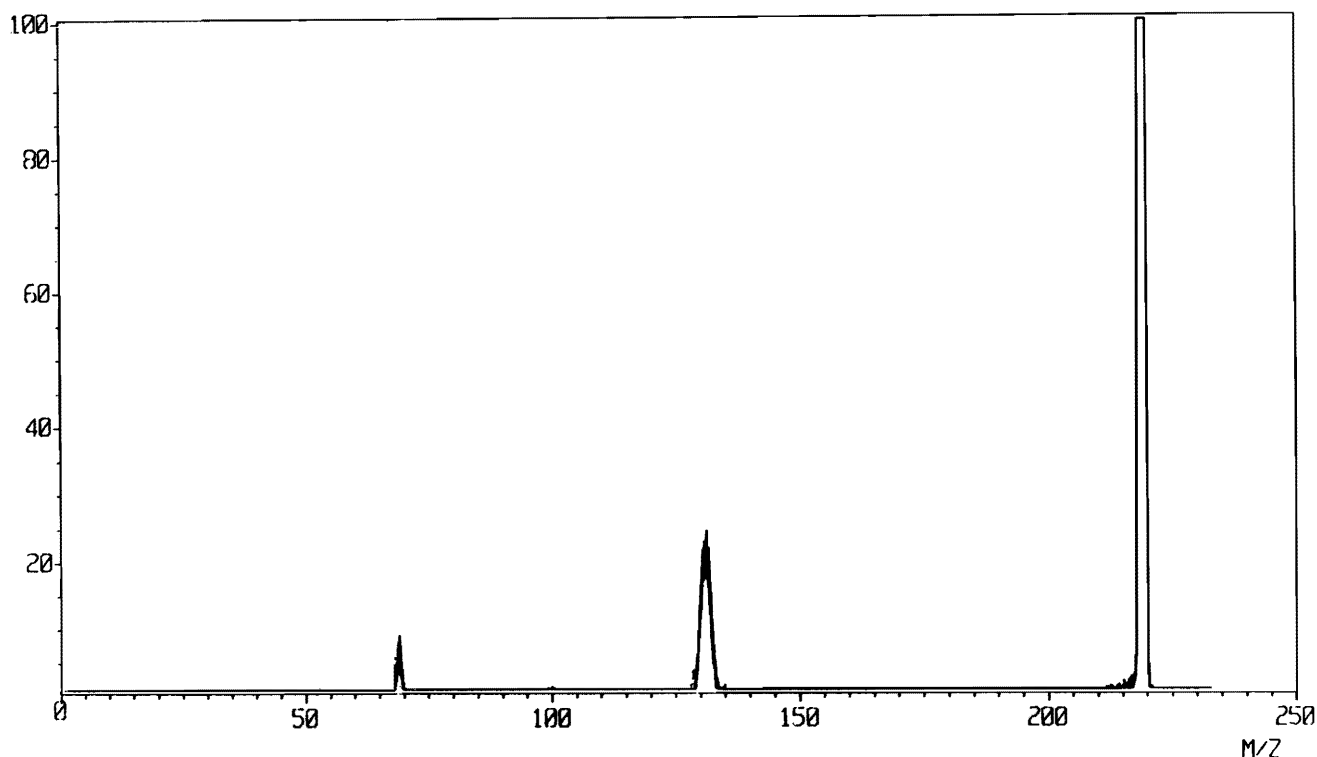
Figure 1. MIKES of 219^+ in PFK Without Collision Cell; Metastable Ion Transition. The Parent Peak is 12% off the Scale.

Since the directions of motion of all the daughter ions coincide with the original directions of motion of the parent ions m_1^{+z1}, they will appear to be issuing from the slit as a mono-velocity beam with the same divergence angle as the original parent ions. An ion of mass-to-charge ratio m_1/z_1 with acceleration voltage V_a from the ion source will approach the collision cell, after being mass-selected by the magnetic field, B, with a velocity v_1 and an energy KE_1 given by

$$KE_1 = m_1 v_1^2/2 = V_a e z_1 \qquad (1)$$

and will be in the cell of potential V_c with an energy KE_1' given by

$$KE_1' = (V_a - V_c) e z_1 . \qquad (2)$$

The mean kinetic energy KE_2' of daughter ions of mass-to-charge ratio m_2/z_2 at the moment of their formation by collision-induced or unimolecular dissociation occurring within the cell will be, according to the above discussion,

$$KE_2' = (V_a - V_c) e z_1 \cdot (m_2/m_1). \qquad (3)$$

After leaving the cell, they are again accelerated (or decelerated) by the floated potential of the cell and the total kinetic energy becomes [5, 6, 9]

$$KE_2'' = KE_2' + V_c e z_2$$

$$= V_a e z_1 \cdot (m_2/m_1) + V_c e(z_2 - z_1 \cdot m_2/m_1) \qquad (4)$$

In the absence of fragmentation, an ion returns its kinetic energy to its original value KE_1 after leaving the cell, through a process of retardation and acceleration by the cell potential. For those daughter ions formed outside the cell (either before or after the cell), their kinetic energy should remain the same fraction, m_2/m_1, as that of the precursor, *i.e.*

$$KE_2 = e z_1 \cdot (m_2/m_1) \qquad (5)$$

which is actually the first term of Equation (4). Thus the influence of floated potential of the collision cell on the kinetic energy of m_2 is the second term of Equation (4) which is, understandably, a function of cell potential and the mass ratio of the daughter—parent ion pair. For those ions fragmented during acceleration or retardation in the vicinity of the cell,
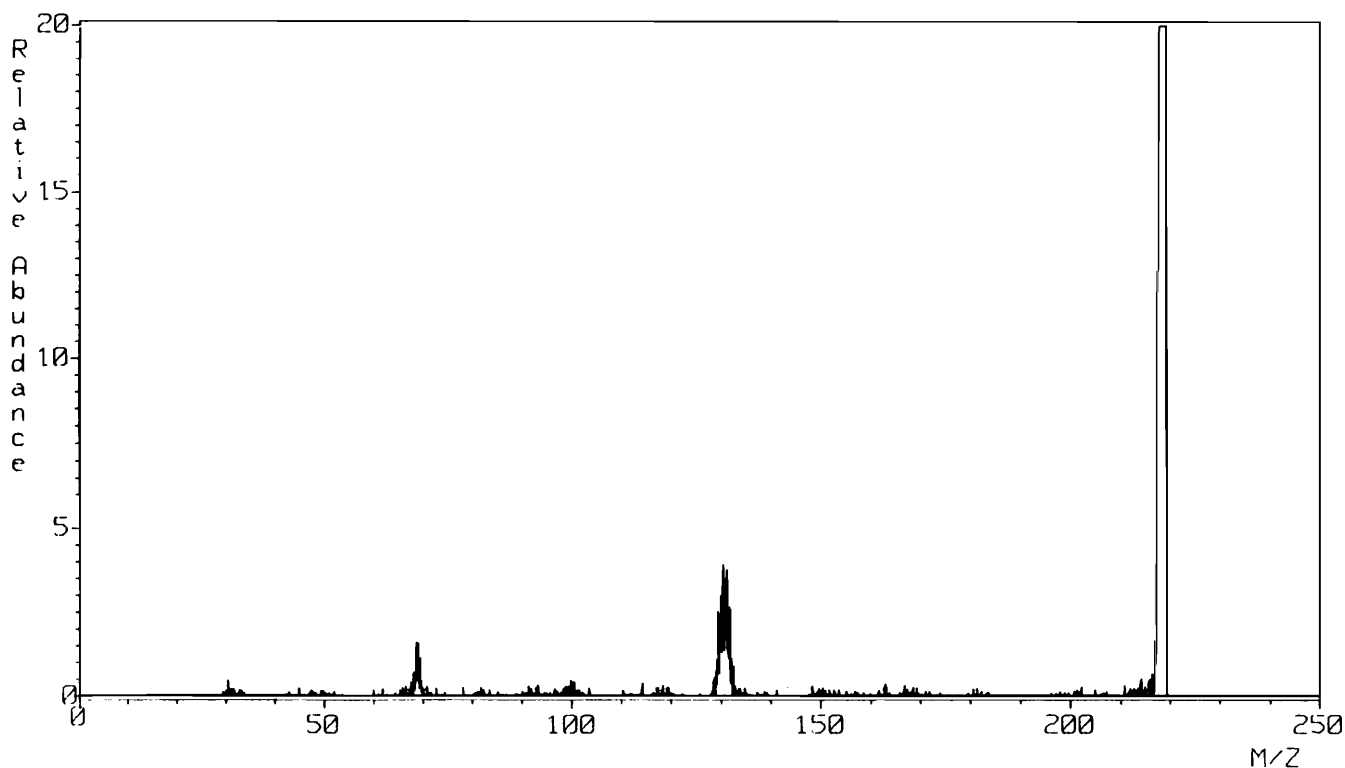
Figure 2. MIKES of 219^+ in PFK with the Collision Cell but no Target Gas; Decrease in S/N is Observed. The Parent Peak Appears Saturated due to the Magnification of Ordinate by a Factor of 5.

their kinetic energy will be intermediate between the value of Equations (4) and (5) and will impart to the broadening of the linewidth of daughter peaks in the MIKES. This equation shows that regardless of whether the fragmentations are through metastable transition or CAD, those occurring inside the cell should be shifted in kinetic energy toward the parent ion if a positive potential is applied to the cell, relative to the stationary peaks which arise from fragmentation occurring outside the cell (See sketch in Figure 3 where the energy scale is based on $m_1/m_2 = 2$ and $V_c/V_a = 0.2$). On the other hand, the daughter peaks shift away from the parent peak if a negative potential exists on the cell. We define the KES as the absolute value of the ratio of second term in Equation (4) to Equation (5):

$$KES = | \ V_c \ e(z_2 - z_1 \cdot m_2/m_1)/(V_a ez_1 \cdot m_2/m_1) \ |$$

$$= | \ V_c/V_a \ | \ (z_2 m_1/z_1 m_2 - 1) \ . \tag{6}$$

Since the kinetic of ions is proportional to the electrostatic field strength and the latter is, in turn, proportional to the mass of the ions in MIKES, Equation (6) simply measures the ratio of the shifted portion to the original position without cell potential on the mass axis from the origin. As the mass of daughter ion becomes smaller, its KES becomes larger.

When helium gas of 10^{-6} torr was admitted to the collision cell without applying the cell voltage, MIKES showed a definite increase in fragmentation of n-dodecane molecular ion rendering the enhancement of lower m/z peaks. Shown in Figure 4 are the MIKES of daughter peaks at their original positions as a result of CAD. As we pointed out in the experimental section, this S/N was roughly seven times better for metastable transition monitored at peak 99^+ without the collision cell, a very good performance of HX100, although in that case the lower mass peaks would be relatively less abundant due to the unimolecular dissociation. As the potential, V_c, of the collision cell was raised to $+1$ kV, the resultant MIKES became that shown in Figure 5 where,
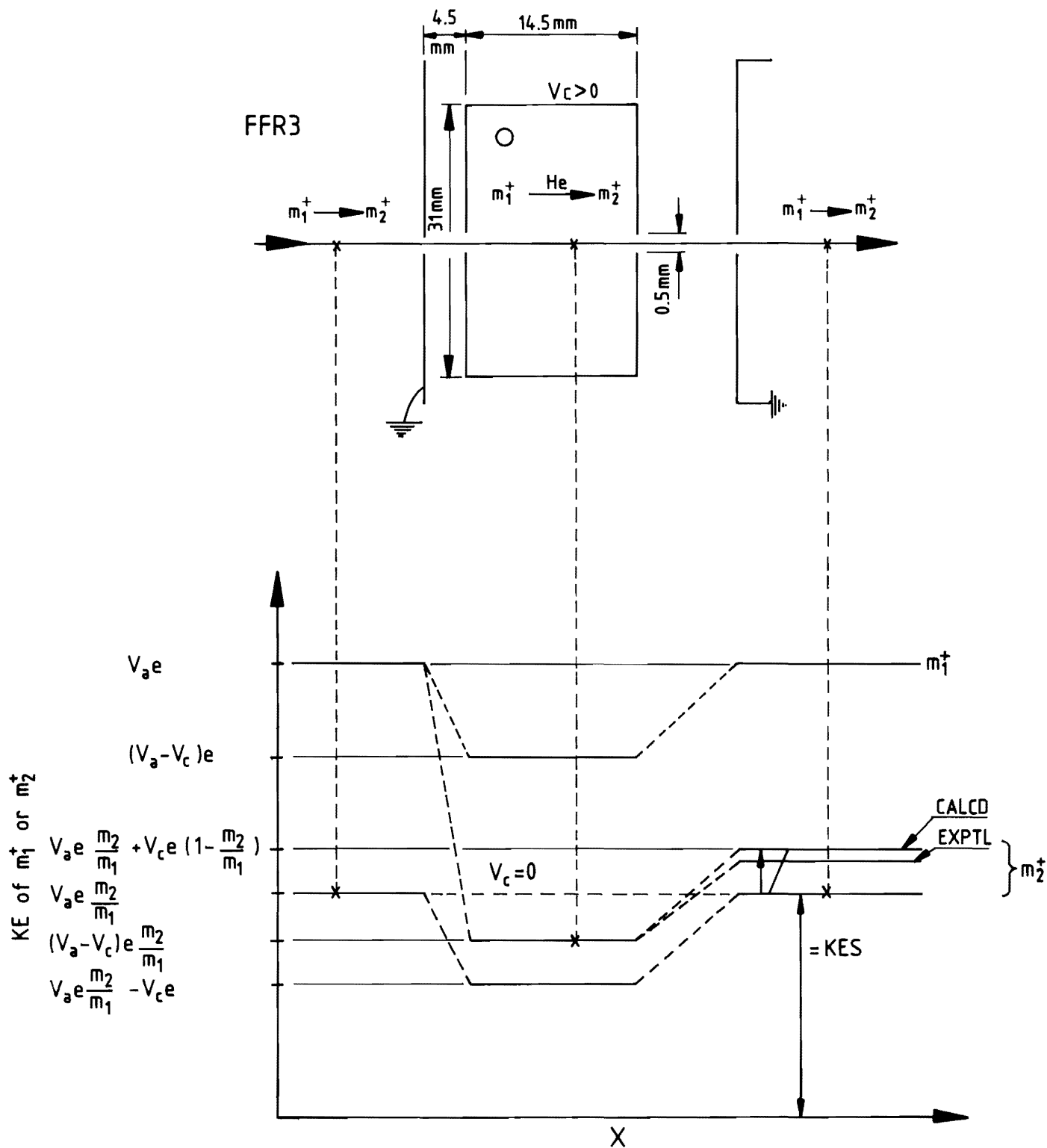
Figure 3. The Calculated Kinetic Energy Diagram of the Ion Beam Inside and Outside the Floated Collision Chamber. The Energy Scale is Based on $m_1/m_2 = 2$, $V_a = 5\,kV$, $V_c = 1.0\,kV$. Note that the Experimental KES are Always Lower than the Predicted Values.
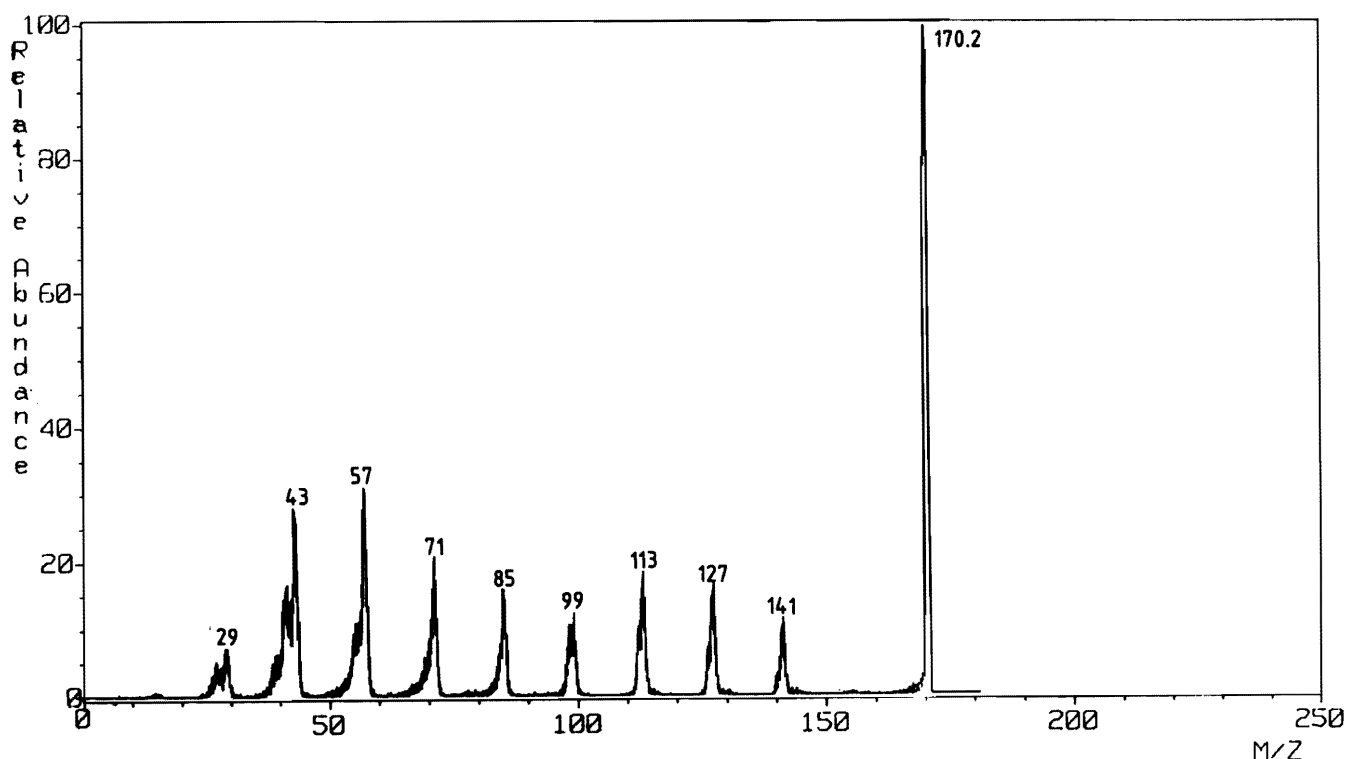
Figure 4. MIKES of 170⁺ in n-Dodecane. $P_{He} = 1 \times 10^{-6}$ torr and $V_c = 0$. No KES is Observed.

for fear of losing sensitivity, more sample was introduced. The arrows in this Figure indicate all the observable daughter peaks in Figure 4 shifted toward the parent peak, *i.e.* higher kinetic energy side, as anticipated by Equation (4). Their calculated $(KES)_{cal}$ and experimental $(KES)_{exp}$ are listed in Table 1. Negative signs in the last column indicate that the experimental kinetic energy shifts are less than those predicted from Equation (6). Since all the peaks are under-shifted, there is no doubt that a good portion (less than 10 percent of the anticipated shift) of the kinetic energy is lost during the collisions. For example, at $m_2^+ = 85^+$, the calculated $(KES)_{cal}$ should be a ratio corresponding to 20 percent of the unperturbed kinetic energy, 2.5 keV, yet the observed is about 1 percent less than the caluculated. Hence 25 eV energy is transfered in the impact, which is equivalent to a 5 percent loss on the $(KES)_{cal}$ scale. This amount of kinetic energy loss contributes not only to the momentum transfer to the target helium molecules; but also to the partitioning of the vibrational–electronical excitation leading to dissociation.

The most probable energy deposition internally can be estimated using Massey's adiabatic criterion [12] to be 0.44 eV for $m_1^+ = 170^+$ at velocity of 7.5×10^6 cm s^{-1} under 5 kV acceleration. Direct vibrational excitation by momentum transfer was reported [8, 9] to be, generally, less than 1 eV. Even in the charge stripping reactions [13] which involve

Table 1. Kinetic Energy Shifts of Daughter Ions from the CAD of n-Dodecane Molecular Ion Under $P_{He} = 10^{-6}$ torr and $V_c = 1$ kV.

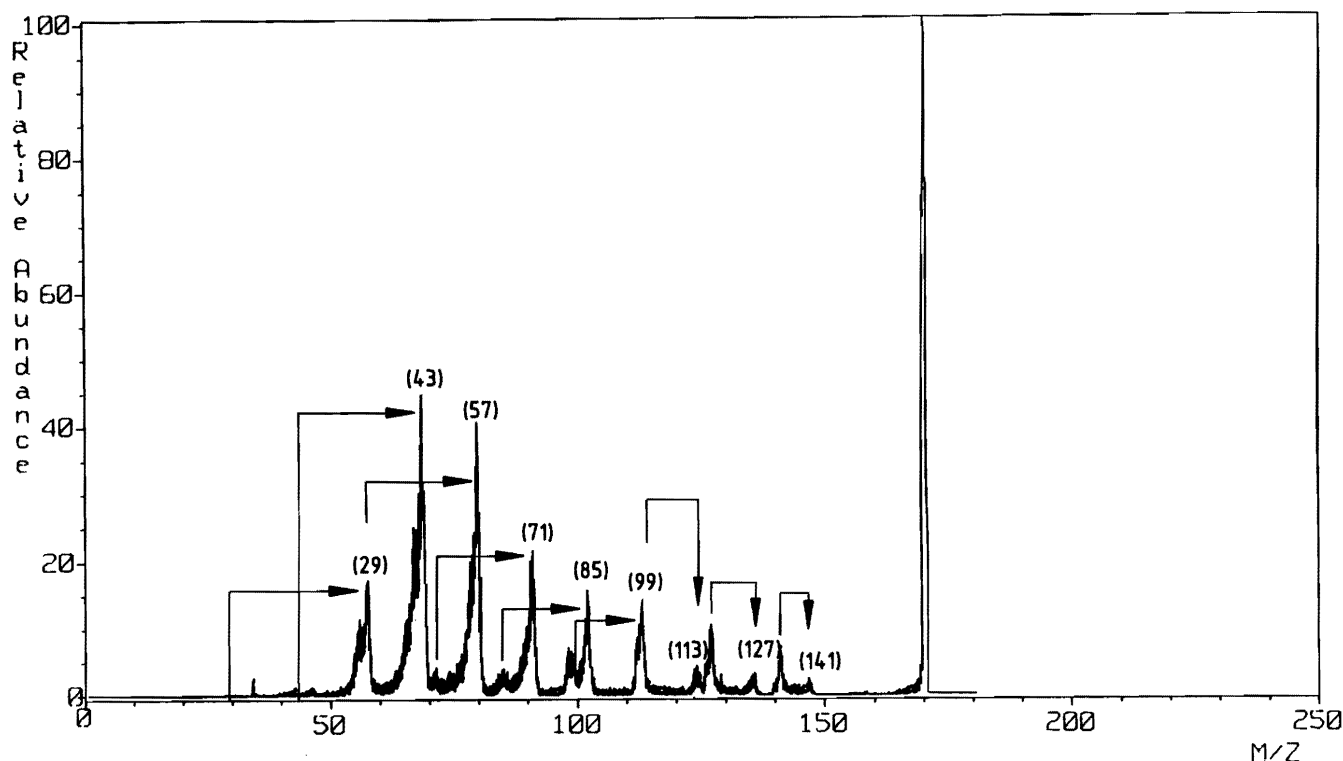| m_2^+	m_1^+/m_2^+	$(KES)_{cal}$ [Equation (6)]	$(KES)_{exp}$	$\Delta(KES)$ Percent
141	1.21	0.042	0.039	−7.1
127	1.34	0.068	0.066	−2.9
113	1.51	0.100	0.095	−5.0
99	1.72	0.140	0.130	−7.1
85	2.00	0.200	0.190	−5.0
71	2.40	0.280	0.270	−3.6
57	2.99	0.400	0.390	−2.5
43	3.96	0.590	0.57	−3.4
29	5.87	0.970	0.940	−3.1

Figure 5. Same as in Figure 4 Except $V_c = +1.0\,kV$. *High-Mass Shifts are Observed.*

electronic excitation CAD process, the most probable experimental energy loss in both benzene and aniline is 16 eV or so. Therefore, both internal energy transfers cannot account for this $\Delta(KES)$. In a series of CAD experiments in which a variety of neutral species having kiloelectron volt translational energies enter a gas cell where they ionize the target gases, the translational energy that the target xenon acquires is less than 0.5 eV and is almost constant for all the projectiles [14]. It seems that the kinetic energy loss in our results is still too large to be attributed to the inelastic scattering [15], although the lighter target helium molecules should take on larger kinetic energies. To understand the scattering process during collision, angle-resolved mass spectrometry with very small scattering angles must be employed. However, the target energy transfer following collision at different angles for various target gases would not vary for over 10 eV [14]. Hence the presumption that the energy partition to daughter ion by the fraction, m_2/m_1, in metastable transition may not be true for CAD. As a consequence of this approximation [6, 9], KES is significantly overestimated for cumene.

Because there are reactions that occur unimolecularly outside the cell and form the same daughter ions, leading to the overlapping of the shifted on the unshifted peaks, a compound with only a few well-separated fragment ions would increase the measurement accuracy. Figure 6 shows that the two daughter ions at 69^+ and 131^+ of 219^+ in PFK were shifted upward when $V_c = +1.0\,kV$ was applied. Again, the experimental KES' are not as large as expected, with few percent differences. It also demonstrates that there are substantial amounts of 131^+ and 69^+ produced outside, as well as inside, the collision cell. One would expect the ratio of the intensity of the unshifted to the corresponding peak due to fragmentations within the cell to be close to the ratio of the length of the field-free region to that of the cell. This ratio is approximately 44 on the HX100. The signal heights in Figure 6 clearly indicate that only five times as much of 131^+ is generated unimolecularly as by CAD, suggesting that the collisional cross-section is significantly larger than the unimolecular dissociation cross-section (see the following section). A low-mass shift spectrum of
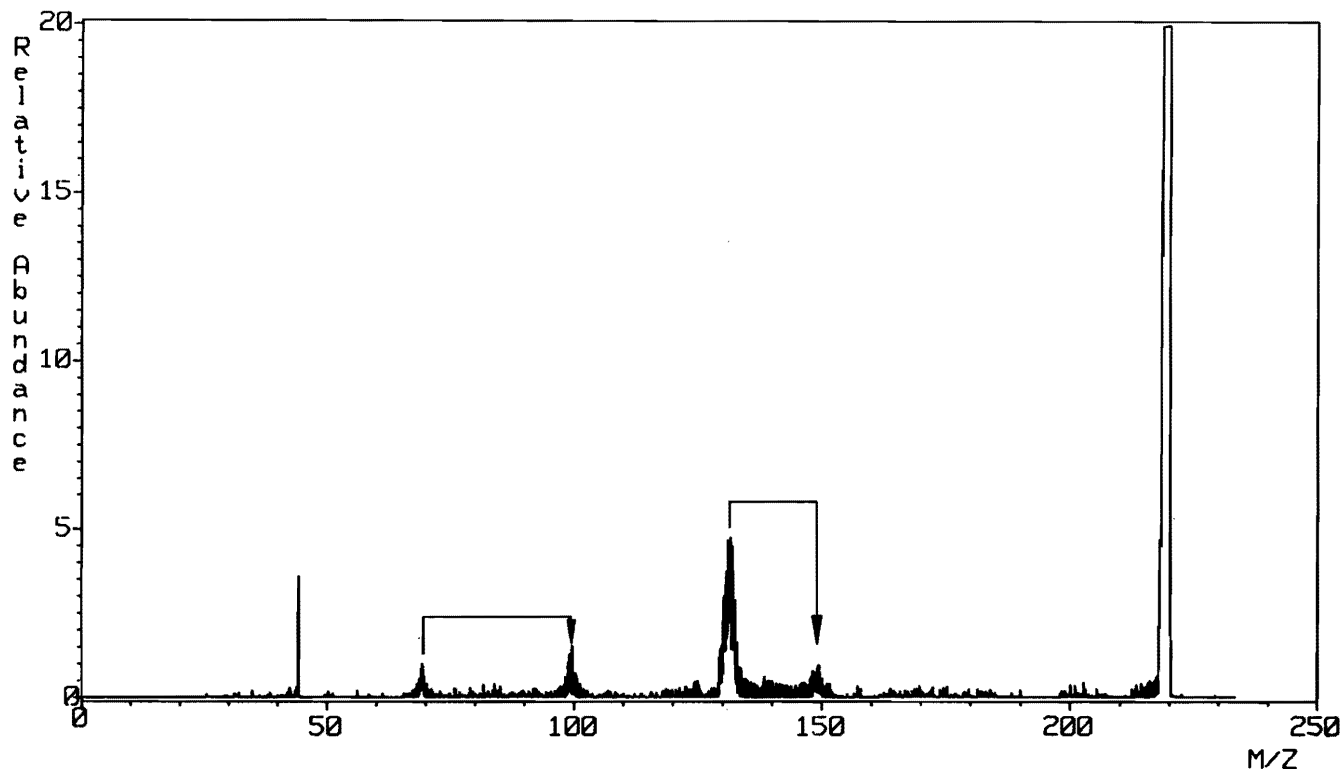
Figure 6. MIKES of 219^+ in PFK. $P_{He} = 10^{-6}$ torr and $V_c = +1.0$ kV. Separation of Metastable Transition from CAD.

n-dodecane is shown in Figure 7 for $V_c = -1.0$ kV as is verified by Equation (4). The shifted peak 29^+ is not observable since its kinetic energy, $V_a e m_2/m_1 + V_c e (1 - m_2/m_1)$, after the collision chamber is almost zero and it is unable to reach the detector. However, the experimental KES' are larger than those calculated in this case (see Figure 8). Namely, the relative position of energy levels in Figure 3 are the same except those inside the collision cell, which should be inverted with respect to $V_c = 0$. In addition, both calculated and experimental KES levels are now below the energy level of m_2^+ at $V_c = 0$, with their relative position unchanged. These results have been further confirmed by using MIKES on $m/z = 219^+$ from PFK at $V_c = -1$ kV and -2 kV.

2. Pressure Dependence of Cumene CAD and its Fragmentation Efficiency

Selected as a suitable compound with both aromatic and aliphatic moieties for fragmentation study, isopropylbenzene gives abundant molecular ions, M^+, with other characteristic peaks at 105^+, 91^+,

77^+, and 51^+, etc. by electron impact. In contrast to low-energy (<100 eV) CAD which involves an initial excitation by direct transfer from translational to internal vibrational energy [16], high-energy (>2 keV) cumene molecular ion CAD is regarded to be electronically excited first [17]. The target gas pressure was varied from nominal vacuum to 10^{-5} torr while MIKES were taken and their corresponding parent ion beam ratio of CAD to metastable transition were monitored on the oscilloscope directly. Let M_0 and M represent the parent ion signal height or area at target pressure $P = 0$ or normal mass spectrometer vacuum where metastable transitions occur, and $P > 0$ where CAD takes place, respectively, and F_i is the signal intensity for fragment ion i at the collector side. The fragmentation efficiency is defined as $E_F = \Sigma F_i/(M + \Sigma F_i)$. Note that M_0 is not the total amount of parent ion before fragmentation or in front of collision cell but is the existing parent ion detected after self-dissociation. Hence when $M = M_0$ at the residual mass spectrometric pressure of less than 10^{-7} torr, fragmentation has already taken place. Summarized in Table 2
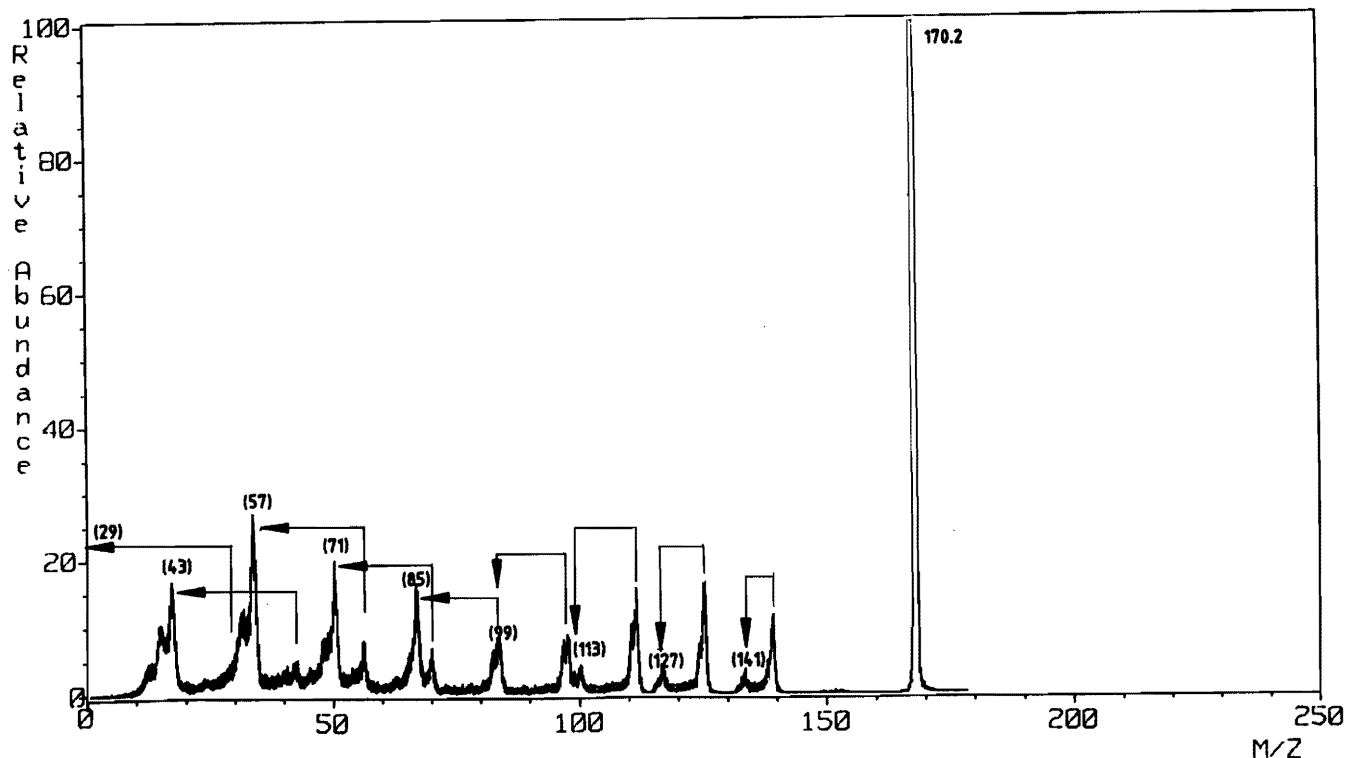
Figure 7. MIKES of 170^+ in n-Dodecane. $P_{He} = 2 \times 10^{-6}$ torr and $V_c = -1.0$ kV. Low-Mass Shifts are Observed.

are the observed fragmentation efficiencies based on the signal heights and the integrated areas under the peaks of MIKES. By this definition, the fragmentation efficiency in the high-energy collision for cumene ranged averagely from 74 percent to 88 percent. This corresponds, respectively, to an estimated fragmentation cross-section of 3.2×10^{-14} to 2.6×10^{-14} cm^2 [9, 12, 14, 18] which is relatively high and reasonable [19]. The only uncertainty here is the actual target pressure inside the collision chamber. Most of the precursor ions, however, underwent an average of one collision at target pressure of less than 10^{-5} torr [20]. The fragmentation efficiency seems to increase as the collision gas pressure is increased. Further increase in pressure would occasionally trigger the vacuum protection system of the instrument to operate, hence no data could be obtained. If a first-order CAD process dependence on collision gas [18] within this pressure range exists: $dM/M = -k dP$, where k is a constant, one would expect a plot of $\ln(M/M_o)$ versus P (as in Figure 9) to be linear. As a matter of fact, a rate constant $k = 0.87 \times 10^6$ torr^{-1} can be extracted from the slope

of this plot within $P \leqslant 3 \times 10^{-6}$ torr. Thus, the fragmentation rate in the collision chamber for cumene molecular ions is quite close to the ion formation rate in the flight path, as was depicted by the modified quasi-equilibrium theory (QET) [21] with similar magnitude of rate constant on time scale. This pseudo-first-order dependence on the target pressure merely reflects that a constant collisional cross-section exists at lower target pressure and most

Table 2. Fragmentation Efficiencies of Cumene CAD Under Various Target Helium Pressure.

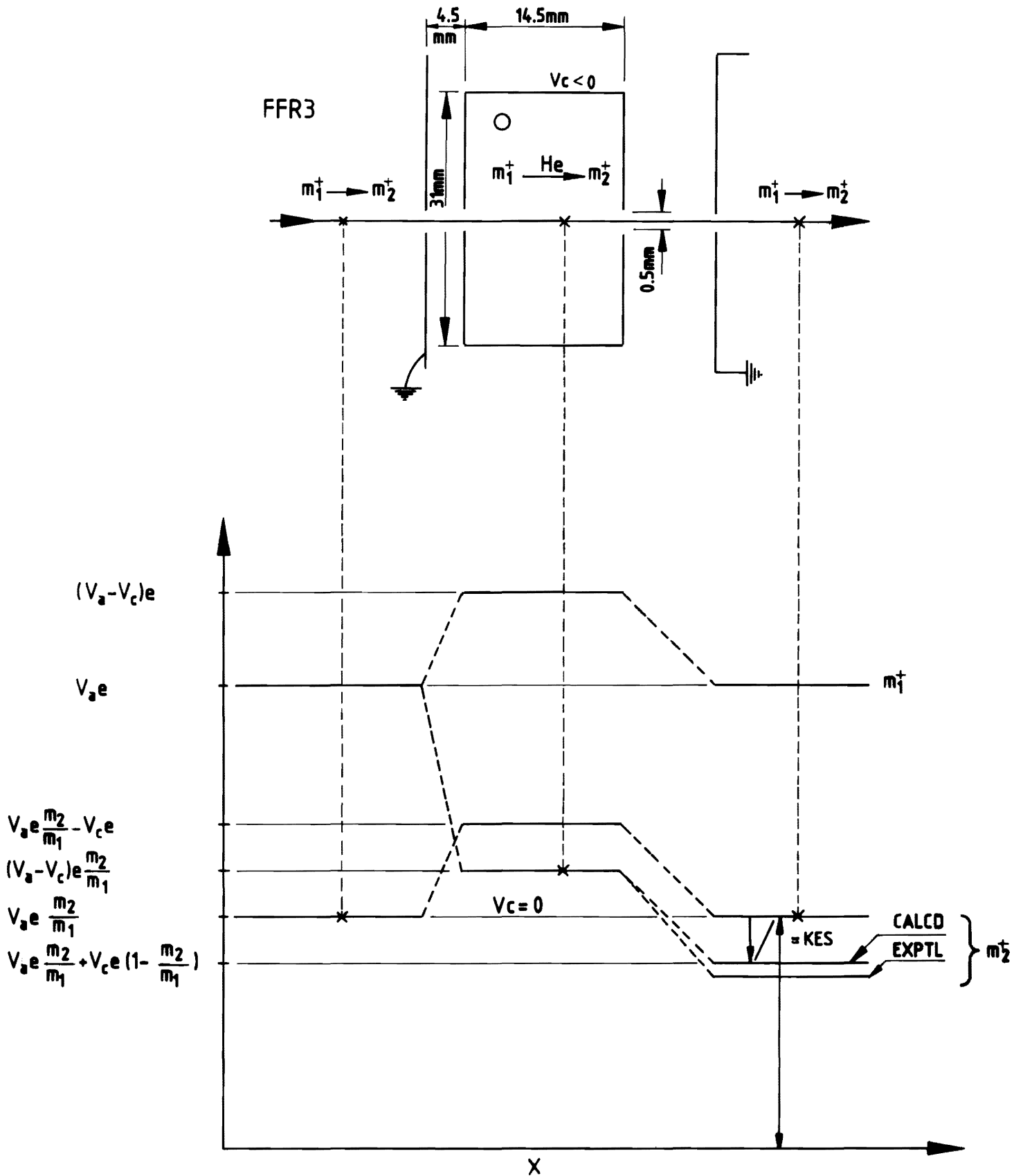| P, Torr	M/M_o	E_F Area	E_F Height
$< 10^{-7}$	1	0.39	0.48
0.8×10^{-6}	1/2	0.74	0.74
2.9×10^{-6}	1/8	0.75	0.74
4.2×10^{-6}	1/16	0.88	0.86
5.3×10^{-6}	1/32	0.85	0.82
6.8×10^{-6}	1/64	0.82	0.70
1.0×10^{-5}	1/1152	0.94	0.81

Figure 8. Same Conditions as in Figure 3 Except $V_c = -1.0\,kV$. *Contrary to* $V_c > 0$, *the Experimental* KES *are Larger than the Calculated Values.*
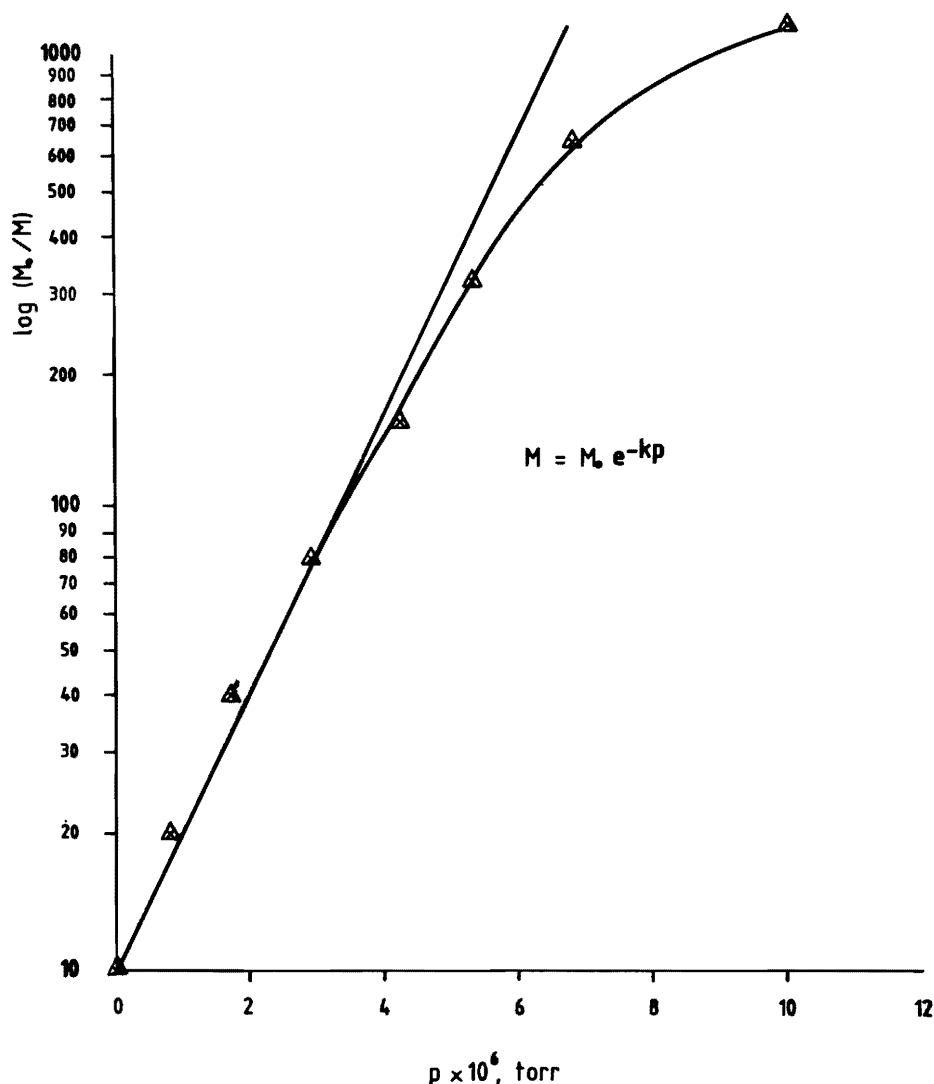
Figure 9. Semi-logarithmic Plot of Cumene Molecular Ion CAD Under Various Collision Gas Pressures.

of the CAD occurs under single collision reaction. As the target pressure increases, the probability of multiple collision increases leading to the different effective collisional cross-sections of the parent ion and thus deviation from linearity.

CONCLUSIONS

KES as defined in this paper provides a new avenue for the study of energy transfer between a precursor ion and a target gas as is demonstrated in this work. Its measurements are found to be accurate to unit electron volt. It is applicable to any double focusing or tandem mass spectrometer equipped with an electrically floatable collision chamber. Increasing in fragmentation efficiency as the collision gas pressure is raised is an indication of a larger internal energy transfer through kinetic

energy loss provided that the activation energy of the dissociation, collisional frequency factor, effective modes of vibration, and others in precursor ion are the same as those in metastable ion. In this aspect, *KES* is similar to the kinetic shift defined in QET or statistical theory of mass spectra. And this is the main rationale that we have defined *KES* in this fashion and carried out the measurements subsequently. However, the two terms are not to be confused with each other—kinetic shift deals only with internal energy during collision. Thus, concomitant study on the *KES* or kinetic energy loss and fragmentation yield for CAD would provide not only information on the nature of transition complex, but also the momentum transfer to the target gas through conservation laws. This will be one of the subjects that intrigues our further investigations.

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